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A MATHEMATICAL MODEL FOR THE STUDY OF THE SOLVENT EXTRACTION OF PARTIALLY HYDROLYZED METAL IONS*

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1. INTRODUCTION

In this paper, a mathematical model is constructed to explore the implications of the shape of an experimentally obtained curve for the extraction of a metal ion from an aqueous medium into an organic phase using a chelating agent. The model studies the reaction as the system becomes more basic under the hypothesis that the concentrations of the ionic species present are normally distributed over specific pH ranges [1]. Results are obtained which provide relationships between the standard deviations and relate these specific standard deviations to a function of the respective means. Since one of the standard deviations can be determined as a function of known physical constants [1], the model provides a mechanism for predicting the paths of the intermediate reactions which occur as the pH is varied.

The primary reaction which occurs involves the solvent extraction of a metal ion M^{+n} from an aqueous solution into an immiscible organic layer using a chelating acid HL. A complex species is formed which is extracted according to the reaction

$$M_a^{+n} + nHL_0 \rightleftharpoons ML_{no} + nH_a^+ \tag{1}$$

where the subscripts a and o denote whether the particular species is present in the aqueous or organic phases respectively.

In studying the solvent extraction of metals, one is concerned with the charge of the metal ion in the aqueous solution just prior to the extraction procedure. Ideally, it should be observed that there is a direct exchange of H^+ ions per positive charge of the metals as it forms the complex species with the chelating agent. The value of n may be determined experimentally by introducing the distribution coefficient,

$$D \equiv \frac{[ML_n]_o}{[M^{+n}]_a} \tag{2}$$

which is the ratio of the total metal concentration in each phase. The square brackets denote concentrations and D is an experimentally measurable quantity.

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Writing an equilibrium expression for (1) yields,

$$K_{ex} = \frac{[ML_n]_o[H^+]_a^n}{[M^{+n}]_a[HL]_o^n}, \tag{3}$$

and the subsequent substitution of (2) into (3) gives

$$D = K_{ex}\frac{[HL]_o^n}{[H^+]_o^n}.$$

Taking logarithms and using the relationship $pH \equiv -\log_{10}[H^+]_a$, one has

$$\log D = \log K_{ex} + n \log [HL]_o + n\text{pH}$$

and consequently,

$$\left(\frac{\partial \log D}{\partial \text{ pH}}\right)_{[HL]_o} = n.$$

Thus a plot of log D vs. pH gives a slope equal to n which is the charge of the metal ion in the aqueous phase. The above plot is feasible since $[HL]_o$ is present in large quantity and remains nearly constant during the course of the reaction. In addition, whatever ML_n forms is completely extracted leaving none in the aqueous phase when equilibrium is reached.

However, it has been observed by several authors [2,3,4] that the slope of the plot of log D vs. pH is not constant, which is particularly evident when the pH of the solution is increased by adding OH^- ion to the solution. In particular, from the reaction

$$H_a^{+n} + OH_a^- \rightleftharpoons MOH_a^{n-1}$$

one can see that the metal ion has become partially hydrolyzed with the addition of OH^- ions to form a new ion, MOH_a^{n-1}, which is now present in the aqueous phase and can also be extracted with HL. Therefore, a second extraction equilibrium reaction can also exist, namely,

$$M(OH)_a^{n-1} + (n-1)HL_o \rightleftharpoons M(OH)L_{n-1} + (n-1)H_a^+. \tag{4}$$

Defining the distribution coefficient

$$D \equiv \frac{[M(OH)L_{n-1}]_o}{[MOH^{n-1}]_a}$$

and using the equilibrium expression

$$K_{ex} \equiv \frac{[M(OH)L_{n-1}]_o[H^+]_a^{n-1}}{[MOH^{n-1}]_a\,[HL]_o^{n-1}}$$

as in (2–3) and proceeding in a similar manner gives

$$\log D = \log K + (n-1)\log [HL]_o + (n-1)\text{ pH}$$

and

$$\left(\frac{\partial \log D}{\partial \text{ pH}}\right)_{[HL]_o} = n-1.$$

Of course, according to the principles of chemical equilibrium both reactions (1) and (4) must exist simultaneously; however, in an acidic solution with pH small, (1) prevails while (4) predominates as the pH increases. The relative concentrations of all four species, M_a^{+n}, $M(OH)_a^{n-1}$, $ML_{n,a}$, $M(OH)L_{n-1,o}$, will vary depending upon H^+ but will be present simultaneously. Such a condition is particularly perplexing to those who are engaged in solvent extraction research as it is difficult to distinguish between the various forms of the species present in each phase by conventional analytical chemical techniques. The proposed model will attempt to explore the relationships between the four species present as the pH is altered.

THE MODEL

The previous discussion demonstrates that any model must account for the presence of concentrations of both the unhydrolyzed metal ion M^{+n} and the hydrolyzed species MOH^{n-1} in the aqueous phase. Consequently, both species ML_n and $M(OH)L_{n-1}$ would be expected to be extracted into the organic phase. Thus the appropriate distribution coefficient would be defined as

$$D \equiv \frac{[ML_n]_o + [M(OH)L_{n-1}]_o}{[M^{+n}]_a + [M(OH)^{n-1}]_a}$$

where

$$\lim_{\text{pH}\to\infty} \frac{\partial \log D}{\partial \text{ pH}} = n-1 \tag{5}$$

and $\dfrac{\partial \log D}{\partial \text{ pH}} \cong n$ for values of pH where hydrolysis is negligible. In this study, we are assuming that the concentrations of species such as $M(OH)L_a$, $ML_{2,a}$, and ML_a^{+1}, are very small and do not play any significant role in the equilibria.

In order to study the behavior of $\partial \log D/\partial$ pH one would like to proceed in a manner similar to that employed for the equilibria of (1) and (3). However, the major obstacle which arises is that even if the reactions of (1) and (3) were combined together as one reaction and the corresponding equilibrium constant K_{ex} defined, it would be impossible to express K_{ex} as a product of D (viz. (5)) and terms independent of the metal M due to the additive nature of the numerator and denominator. Therefore, another approach needs to be sought.

Previous work by Graff and Berger [1] shows that it is plausible to hypothesize the dependence of H^{+n} upon pH to be of the form

$$[H^{+n}]_a = \begin{cases} A\, e^{-\alpha(x - x_0)^2}, & x \geq x_0,\ A > 0,\ \alpha > 0 \\ A, & x < x_0,\ A > 0 \end{cases} \tag{6}$$

where $x \equiv$ pH which is the right half of a normal distribution with mean x_0 for $x \geq x_0$ and is constant for $x < x_0$. The value of x_0 is chosen to be the level of pH at which the

depletion of the H^{+n} ion is deemed to become significant with respect to a criterion chosen prior to the experiment. Similarly, one also has

$$[H(OH)^{n-1}]_a = Ce^{-\gamma(x - x_2)^2}, \quad C > 0, \quad \gamma > 0 \tag{7}$$

A detailed discussion is found in [1] but a summary is presented in the appendix.

The ramifications of (6) and (7) are seen by considering the extreme situations small or large pH which is described by (1) and (2) or (3) and (4) respectively. In either case, $\partial \log D/\partial$ pH is approximately constant and (2) and (4) therefore imply that the dependence of $[H_n]$ and $[MOHL_{n-1}]$ upon $x \equiv$ pH must also be exponential, namely,

$$[HL_n]_o = Be^{-\beta(x-x_1)^2}, \quad B > 0, \quad \beta > 0 \tag{8}$$

and

$$[H(OH)L_{n-1}]_o = Ee^{-\epsilon(x-x_2)^2}, \quad E > 0, \quad \epsilon > 0. \tag{9}$$

Ordinarily, the linear dependence of $\log D$ upon pH in each of the simple situations would also force $\alpha = \beta$ and $\gamma = \epsilon$ as well; however, one cannot conclude from this that $\alpha = \beta$ or $\gamma = \epsilon$ since the experimentally obtained plots of $\log D$ vs. pH are not linear for pH values which are neither small nor large. Eventually, it will be shown that $\beta \geq \alpha = \gamma = \epsilon$ but these relationships follow from other considerations.

Lastly, the ordering of the means x_j, $0 \leq j \leq 3$, of the normal distributions in (6–9) remains to be considered. In each of the simple cases given by (1) and (3), it is plain that the form of the metal ion in the aqueous state on the left hand side will attain its maximum concentration before the extracted species on the right hand side does. Hence

$$x_0 < x_1 \quad \text{and} \quad x_2 > x_3.$$

Furthermore, the equilibrium (3) only begins to dominate after a sufficient amount of the metal H^{+n} is hydrolyzed implying that HL_n will achieve its maximum level before $(OH)^{n-1}$ does; in other words, $x_1 < x_2$, and therefore

$$x_0 < x_1 < x_2 < x_3.$$

To summarize the entire situation, Fig. 1 illustrates the hypotheses regarding the four species H^{+n}, HL_n, MOH^{n-1}, and $M(OH)L_{n-1}$ while Fig. 2 depicts the hypothesis on $\log D$.

The intent of the subsequent calculations is to first deduce the implications of the conditions

$$\lim_{\text{pH}\to\infty} \partial \log D/\partial \text{ pH} = n-1$$

and

$$x_0 < x_1 < x_2 < x_3$$

by substituting (6–9) into (5). In order to simplify the computations x_0 is set equal to zero. In the case that $x_0 \neq 0$ one need only replace x by $x - x_0$ in the ensuing formulas. Proceeding

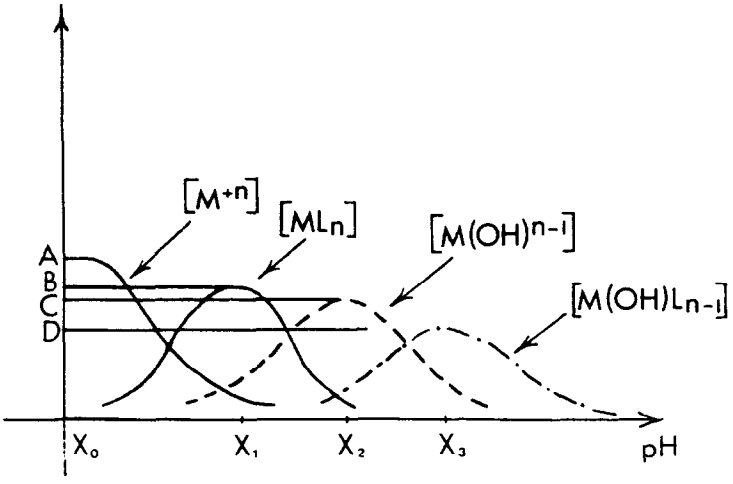

Fig. 1. Distributions of the four species as a function of pH

formally,

$$D = \frac{Be^{-\beta(x-x_1)^2} + Ee^{-\epsilon(x-x_3)^2}}{Ae^{-\alpha x^2} + Ce^{-\alpha(x-x_2)^2}},$$

$$\log D = \log [Be^{-\beta(x-x_1)^2} + Ee^{-\epsilon(x-x_3)^2}] - \log [Ae^{-\alpha x^2} + Ce^{-\gamma(x-x_2)^2}],$$

$$\frac{\partial \log D}{\partial \text{ pH}} = -2\frac{\beta B(x-x_1) + \epsilon E(x-x_3)\, e^{\beta(x-x_1)^2-\epsilon(x-x_3)^2}}{B + E\, e^{\beta(x-x_1)^2-\epsilon(x-x_3)^2}} + 2\frac{\alpha Ax + \gamma C(x-x_2)\, e^{\alpha x^2-\gamma(x-x_2)^2}}{A + Ce^{\alpha x^2-\gamma(x-x_2)^2}}$$

The behavior of $\partial \log D / \partial$ pH for large pH is determined by the relative magnitudes of the growth rates α,β,γ, and ϵ. In particular, nine cases arise and are enumerated in Table 1. The necessary conditions for $\lim_{\text{pH}\to\infty} \partial \log D / \partial \text{ pH} = n - 1$, the region where more significant hydrolysis occurs, are found in Table 2. It now follows from the hypothesis $x_0 = 0 < x_1 < x_2 < x_3$ that cases 2*b*, 2*c*, 3, 5*b*, 5*c*, 6, 8*b*, and 8*c* are untenable with the

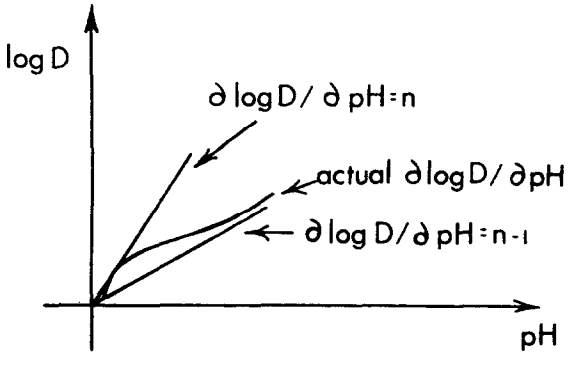

Fig. 2. An idealized plot of log *D* vs. pH for the solvent extraction of metal ions.

Table 1. Possible relative magnitudes for α, β, γ, and ϵ.

(1) $\beta > \epsilon$ $\alpha > \gamma$	(4) $\beta > \epsilon$ $\alpha = \gamma$	(7) $\beta > \epsilon$ $\gamma < \gamma$
(2) $\beta = \epsilon$ $\alpha > \gamma$	(5) $\beta = \epsilon$ $\alpha = \gamma$	(8) $\beta = \epsilon$ $\alpha < \gamma$
(3) $\beta < \epsilon$ $\alpha > \gamma$	(6) $\beta < \epsilon$ $\alpha = \gamma$	(9) $\beta < \epsilon$ $\gamma < \gamma$

assumption that the parameters α, β, γ, ϵ are positive constants. In other words, the only admissible possibilities are 1, 2*a*, 4, 7, 8*a*, and 9.

Referring to the results in the appendix which relate to the hydrolysis of the metal ion, one has $\alpha = \gamma$. Therefore, only cases 4 and 5*a* remain implying

$$\beta \geq \alpha = \gamma = \epsilon = (n - 1) / 2(x_3 - x_2) \tag{10}$$

Lastly, it remains to determine if there are sufficient conditions compatible with (10) for which $\partial \log D/\partial \text{ pH}\,|_{\text{pH}=0} < n$.

The expression for $\partial \log D / \partial \text{ pH}$ yields

$$\begin{aligned}\left.\frac{\partial \log D}{\partial \text{ pH}}\right|_{\text{pH}=0} &= 2\,\frac{\beta B x_1 + \epsilon E x_3\, e^{\beta x_1^2 - \epsilon x_3^2}}{B + E\, e^{\beta x_1^2 - \epsilon x_3^2}} \\ &\quad - 2\,\frac{\gamma C x_2\, e^{-\gamma x_2^2}}{A + C e^{-\gamma x_2^2}} \\ &< 2\,\beta x_3.\end{aligned}$$

Plainly, it suffices to have $2\beta x_3 < n$ or $\beta < n/2x_3$. Together with (10) this implies that β must satisfy

$$\frac{(n-1)}{2(x_3 - x_2)} < \beta < \frac{n}{2x_3}$$

and such an interval is realizable provided $\beta < 1/2x_2$.

Table 2. Relative growth rates for the condition where significant hydrolysis obtains, $\lim_{\text{pH}\to\infty} \partial \log D/\partial \text{ pH} = n - 1$.

Case	
1.	$\gamma = \epsilon = (n - 1)/2(x_3 - x_2)$
2a.	$x_1 < x_3$: $\beta = \gamma = \epsilon = (n - 1)/2(x_3 - x_2)$
2b.	$x_1 = x_3$: $\beta = \gamma = \epsilon = (n - 1)/2(x_3 - x_2) = (n - 1)/2(x_1 - x_2)$
2c.	$x_1 > x_3$: $\beta = \gamma = \epsilon = (n - 1)/2(x_1 - x_2)$
3.	$\beta = \gamma = (n - 1)/2(x_1 - x_2)$
4.	$\alpha = \gamma = \epsilon = (n - 1)/2(x_3 - x_2)$
5a.	$x_1 < x_3$: $\alpha = \beta = \gamma = \epsilon = (n - 1)/2(x_3 - x_2)$
5b.	$x_1 = x_3$: $\alpha = \beta = \gamma = \epsilon = (n - 1)/2(x_3 - x_2) = (n - 1)/2(x_1 - x_2)$
5c.	$x_1 > x_3$: $\alpha = \beta = \gamma = \epsilon = (n - 1)/2(x_1 - x_2)$
6.	$\alpha = \gamma = \beta = (n - 1)/2(x_1 - x_2)$
7.	$\alpha = \epsilon = (n - 1)/2x_3$
8a.	$x_1 < x_3$: $\alpha = \beta = \epsilon = (n - 1)/2x_3$
8b.	$x_1 = x_3$: $\alpha = \beta = \epsilon = (n - 1)/2x_1 = (n - 1)/2x_3$
8c.	$x_1 > x_3$: $\alpha = \beta = \epsilon = (n - 1)/2x_1$
9.	$\alpha = \beta = (n - 1)/2x_1$

CONCLUSIONS

It is shown by Graff and Berger [1], that the parameter α may be calculated from known physical constants,

$$\alpha = \frac{0.6924}{(-\log K_f \cdot K_w + \log [H_o^+])^2}.$$

In particular, K_f is a determined constant for the extraction system and K_w is the dissociation constant for H_2O. In order to develop a relationship between $[M^{+n}]_a$ and $[M(OH)^{n-1}]_a$, a ratio of the two concentrations is employed. The $[M(OH)^{n-1}]_a$ becomes difficult to detect when its concentration is 10^{-6} moles/liter and justifies the ratio of 10^6 since one might begin the experiment using an initial value for $[M^{+n}]$ of 1 mole/liter. The value of $[H_o^+]$ is the concentration of hydrogen ion necessary to achieve $[M^{+n}]_a/[M(OH)^{n-1}]_a = 10^6$; using (13), in the appendix, one then has

$$[H_o^+] = 10^6 \cdot K_f \cdot K_w.$$

Therefore, it follows from (10) that the parameters α, γ, ϵ, and the distance $x_3 - x_2$ may be found in terms of constants of the extraction process. The parameters α, γ, and ϵ are significant in that they determine the standard deviations of the normal distributions representing the concentrations of M^{+n}, $M(OH)^{n-1}$, and $M(OH)L_{n-1}$, and hence allow for the estimation of the length of the interval on the pH axis where these concentrations occur with significance. In addition, from $\beta \geq \alpha = \gamma = \epsilon$ it follows that $\sigma_\beta^2 \leq \sigma_\alpha^2 = \sigma_\gamma^2 = \sigma_\epsilon^2$ since each growth rate α, β, γ and ϵ is equal to $1/2\sigma^2$ where σ symbolizes the respective standard deviations. Furthermore, σ_β which corresponds to the standard deviation of the normal distribution for the species $ML_{n,o}$ is less than that of the other three implying it occurs over a smaller pH range. From (10) it can be seen that the standard deviations for the other species are given by the relationship

$$\sigma_\beta^2 \leq \sigma_\alpha^2 = \sigma_\gamma^2 = \sigma_\epsilon^2 = \frac{x_3 - x_2}{n-1} \tag{11}$$

where $n - 1$, x_2, and x_3 are the charge and the respective means of the normal distributions of the hydrolyzed species MOH^{n-1} and $M(OH)L_{n-1}$. Thus, the presence of hydrolysis plays an important role in determining the pH range for the nonhydrolyzed species as well.

APPENDIX

The Dependence of $[M^{+2}]$ *upon* pH

One of the equilibria which persists during the extraction process is the addition of the hydroxide ion OH^{-1} to the metal ion M^{+2} symobilized by the equation

$$M_a^{+2} + OH_a^{-1} \rightleftharpoons M(OH)_a^{+1}.$$

The classical chemical equilibrium theory postulates the existence of an equilibrium for-

mation constant K_f such that

$$K_f = \frac{[M(OH)^{+1}]_a}{[M^{+2}]_a [OH^{-1}]_a} \tag{12}$$

which is the only equation which specifically links the concentrations of these three species. Since the concentration of the hydroxide ion is always related to the concentration of the hydrogen ion by the relationship

$$K_w = [H^+]_a [OH^{-1}]_a,$$

one frequently expresses the equilibrium (12) in terms of $[H^+]_a$,

$$K_f K_w = \frac{[M(OH)^{+1}]_a [H^+]_a}{[M^{+2}]_a} \tag{13}$$

where K_w is the equilibrium constant for the dissociation of water. The constants K_f and K_w are determined experimentally and assumed to be known.

Using the definition of $pH \equiv -\log_{10} [H^+]$ and (13), it is possible to express the ratio $[M^{+2}]_a/[OH^{-1}]_a$ as an exponential function,

$$\frac{[M^{+2}]_a}{[M(OH)^{+1}]_a} = \frac{1}{K_f K_w} 10^{-pH} = \frac{1}{K_f K_w} e^{-pH/\log_{10} e}. \tag{14}$$

The exponential term of the right hand side of (14) motivates the hypothesis regarding the dependence of $[M^+]_a$ and $[M(OH)^{+1}]_a$ upon pH. Since the quotient of the two quantities must be exponential, one might assume they each have the form

$$[M^{+n}]_a = \begin{cases} A\, e^{-\alpha(x-x_0)}, & x \geq x_0, \\ A, & x < x_0; \end{cases}$$
$$[M(OH)^{n-1}]_a = C\, e^{-\gamma(x-x_1)}$$

with $x_0 < x_1$ and $x = pH$. However, such an assumption is not adequate since for $x_0 < x$ one has

$$\frac{[M^{+n}]_a}{[M(OH)^{n-1}]_a} = \frac{A}{C} \exp\{(\gamma-\alpha)x + (\gamma x_1 - \alpha x_0)\}$$

implying that the ratio would be constant for $\alpha = \gamma$ which is a realizable possibility.

The next most obvious hypothesis is to assume a dependence of the type

$$[M^{+n}] = \begin{cases} A\, e^{-\alpha(x-x_0)^2}, & x \geq x_0, \\ A, & x < x_0; \end{cases}$$
$$[M(OH)^{n-1}] = C\, e^{-\gamma(x-x_1)^2} \tag{15}$$

with $x_0 < x_1$ which precludes the difficulty above when $\alpha = \gamma$. Furthermore, since

$$\frac{[M^{+n}]_a}{[M(OH)^{n-1}]_a} = \frac{A}{C} \exp\{(\gamma-\alpha)x^2 + 2(\alpha x_0 - \gamma x_1)x + \gamma x_1^2 - \alpha x_0^2\}, \quad x_0 < x_1,$$

one can argue that α always equals γ for then the quotient $[M^{+n}]/[M(OH)^{n-1}]$ has the correct behavior. Observe that the expressions in (15) utilize the right half of a normal distribution with mean x_0 and a normal distribution with mean x_1 respectively. Hence, the most elementary hypothesis for the dependence of $[M^{+n}]_a$ and $[M(OH)^{n-1}]_a$ upon pH is that of a normal distribution.

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